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LUBRICANTS AND MECHANICAL COMPONENTS OF LUBRICATION SYSTEMS FOR A SPACE ENVIRONMENT

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STATEMENT OF PROBLEM

In present and future devices, bearings and other load bearing sur-
faces, including movable joints, must be capable of a wide variety of duty
cycles for extended time periods in space environment without the weight
penalty of sealed systems (refs. 1 and 2). Conventional lubricants may
not be useful for extended time periods because of evaporation or disso-
ciation at low pressures (refs. 3 to 7). Conventional thin-film lubrica-
tion practice utilizes normal oxide films on metallic surfaces; when ini-
tial oxide films are worn away, ruptured, dissociated, or otherwise removed
from bearing surfaces in oxygen-deficient environments such as space, con-
ventional organic and other lubricants cease to function in the usual man-
ner (ref. 8). Furthermore, when the lubricant and the normal protective
oxide films are removed, most metals except those immiscible in the liquid
state (refs. 9 to 11) are subject to interface welding during sliding and
rolling. Thus, low pressure and lack of oxygen are the two primary fac-
tors in space environment that make lubrication problems difficult. In
large devices, where circulating liquid systems are required, zero gravity
could be a problem; it is not inherent to thin-film lubrication processes,
however. Space radiation levels are not sufficient to cause degradation
of lubricating and bearing materials that meet other criteria for space
devices. Higher temperatures ($<500^\circ$ F), nuclear radiation, and environ-
ments of thermodynamic working fluids (e.g., liquid metals and cryogenic
fuel or oxidants) provide special problems not treated herein.

The primary problem of concern is one of selecting designs and lubri-
cating materials that will not suffer prohibitive evaporation or disso-
ciation and will function to separate surfaces in relative motion with low
shear force (friction); mechanical parts should be made of materials hav-
ing minimum susceptibility to surface welding. Special design considera-
tion must be given to the difficult problems of dissipating frictional
heat from devices operating in vacuum as well as of minimizing heat gener-
ation.

REVIEW OF STATE OF THE ART

Reduced atmospheric pressures experienced during operation of liquid
rocket engines caused lubrication problems in early ballistic missiles.
Degassing and foaming of organic lubricants at the low pressures (175,000 ft
pressure altitude) impaired lubricating and cooling effectiveness. Some
early bearing failures were attributed to the foaming, but other design and
lubrication factors were probably of predominant importance.

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Initial space lubrication applications have been concerned with lightly loaded bearings with both rotating and oscillating motion in devices launched into low orbits around the Earth. Bearings were of conventional materials and used common lubricants that benefited by restricted evaporation through the use of molecular flow seals.

From both laboratory experiments and bearing applications in satellite experiments, two primary approaches to the problem of lubrication in bearings and movable joints have been found to be usable. First, the systmes concept provides for the operation of conventional lubricants and materials in sealed systems. Where low-vapor-pressure organic lubricants are used and the seal problem is in the regime of molecular flow with modest temperatures ($<200°$ F), significant endurance can be achieved for lightly loaded bearings. The radiometer bearings in Tiros II offer a good example of this system concept (ref. 12). Because seal leakage is a function of pressure ratio in the regime of pressure flow, complex sealing assemblies are required where pressurized systems must be sealed against space environment for extended periods of time.

Second, the materials concept requires the selection of stable materials for use in direct exposure to space environment. Also, the design of bearings and other load-carrying devices must include special provision for removal of heat from friction and other sources. Heat complicates the problem of degradation of lubricating materials. Films of inorganic compounds (e.g., MoS_2, WS_2, WSe_2, etc.), soft metals (Ag, Au, etc.), solid polymers (polytetrafluoroethylene, PTFE, polychlorotrifluoroethylene, PCFE, polyimide, etc.), and liquid metals (e.g., gallium) have low vapor pressures and can provide lubrication for extended periods of time in direct exposure to vacuum (refs. 1, 3, and 13 to 25). Any preformed film will have a finite endurance life that can be adversely affected by the evaporation tendencies and reduced heat transfer that are characteristic of vacuum operation. In regard to heat dissipation, the polymers require special consideration because of poor heat-transfer properties. In the interest of extended endurance lives, solid materials including a lubricating constituent in the structure can be useful (refs. 20 and 21). For example, the use of filled compositions for retainers of rolling-contact bearings, for ball sockets used in gimbal bearings, for idler gears to reform films on operating gears, and for sliding bearings can be useful. A similar statement could probably be made for many solids including a lubricating constituent.

For many years surface reservoirs have proven useful in the application of solid lubricating materials such as graphite. Most recently it has been used effectively with an MoS_2 - graphite mixture for retainers of rolling-contact bearings (ref. 23). In this design consideration, surface recesses of various configurations are machined or otherwise formed on load-bearing surfaces and subsequently filled with a lubricant, such as MoS_2, and a bonding agent, such as a resin or an inorganic compound.

The general practice in forming bonded solid lubrication films with materials such as MoS_2 is to roughen the surface prior to application. The methods used include vapor or grit blasting, chemical etching, and the formation of transition films by surface reaction products (e.g., phosphates) that have a rough texture. The use of such roughened surfaces improved endurance life. The use of surface reservoirs mentioned previously represents an extension of the surface roughening technique. Bonding agents for solid lubricants represent a large gamut of organic resins and inorganic compounds as well as metals in complex formulations. Phenolic and epoxy resins and sodium silicate are most commonly used. The best of these represent but marginal improvements over the less sophisticated use of carbonized corn syrup as suggested in 1946 by Norman (ref. 26) and studied by NACA (ref. 27).

Thin-film lubrication by gallium (ref. 15) is an interesting concept with potential value. Much research and development data are needed in this area. Problems exist as to the optimum method of application and the best materials for lubrication.

Little has been done to develop optimum bearing materials and designs for vacuum operation. The performance of solid lubricants can be improved by proper selection of bearings materials (ref. 24). Design configuration for minimum heat generation and optimum heat dissipation are desirable (ref. 1). Conditions of operation such as vibration have been shown to influence the behavior of bearings in vacuum (ref. 28). .

In the area of selection of bearing materials with least probability for harmful surface welding, certain alloys such as the cobalt alloy Stellite Star-J, have useful properties (ref. 29). These properties may result from stable compounds present as inclusions in those alloys. Such compounds replace the normal surface oxides as they are worn away. Almost any combination of clean metals will show surface welding tendencies during sliding contact; both mechanical adhesion and alloying can be obtained at the interface when complete films of lubrication or other surface contaminants like oxides cannot be maintained. Strong junctions can be established by (1) interface diffusion or alloying, and (2) mechanical adhesion from interlocking of surface irregularities. During relative motion, cold welding can occur even at cryogenic temperatures (ref. 30). Surface adhesion is a fundamental factor in all lubrication processes according to the most widely accepted and studied concepts of friction between solid surfaces (ref. 8).

The occurrance of surface welding is much less apt to occur in the absence of relative motion between surfaces. Significant adhesion studies have been made in air where surface shear from relative motion (e.g., 180°) was used with loaded annular (or rod ends) specimens to rupture surface films such as oxides (ref. 31). Surface shear (1) strips off surface barbiers, (2) roughens surfaces, (3) produces a work-hardened zone just below

the surfaces (4) causes denuded metals to come into atomically close contact, (5) buries the surface barrier debris below the surface, and (6) causes interpenetration of the two metals. It has been shown that even in air surface shear strains can cause very high adhesion that is comparable to that produced between denuded metals in very high vacuum (ref. 32). Solid solubility and interfacial energies have been used as bases for predicting adhesion, but even more fundamental is the atomic size factor. This concept suggests that where atomic diameters of metals differ by more than ±15 percent, surface adhesion will be minimum (ref. 33). Furthermore, it has been shown that metals having large elastic moduli, hardness, surface energy, recrystallation temperature, and resistance to plastic flow are characterized by low coefficients of adhesion. Also metals that crystallize in the cubic structure have a higher tendency to stick than those with hexagonal close-packed structure.

Much of the data available in the literature on vacuum adhesion, friction, wear, and lubrication studies is open to serious question. Back migration of diffusion pump oils and condensates from other sources, such as electrical insulation, contaminate experimental surfaces and invalidate the data obtained. Other data obtained with clean surfaces in air are frequently more meaningful. The danger of accepting data from contaminated vacuum systems is that potential problems can be masked by contaminating diffusion pump oil. No source of diffusion pump oil exists in the space vacuum system.

Most organic fluid and grease lubricants that would be considered for space applications can be used to total radiation dosages of 10^{10} ergs per gram of carbon with less than 10 percent change in viscosity of the base fluid at 210° F (ref. 34). Selected fluids, such as polyphenyl ethers, are useful after significantly greater dosage. Inorganic lubricants have still greater stability. The most severe types of space radiation are associated with the Van Allen belt (ref. 6) where radiation levels to 100 roentgens per hour have been detected and the possibility of 1000 roentgens per hour suggested. At the maximum flux suggested (1000 roentgens/hr), 100,000 hours would be required to achieve a radiation dosage of 10^{10} ergs per gram as mentioned above. Thus, space radiation should not be a problem for lubricants. It should be cautioned, however, that the radiation levels associated with nuclear reactors do provide a problem in lubricant stability. Radiation stability is further improved by the absence of oxygen, which makes it possible to consider the use of such materials as polytetrafluoroethylene base compositions for bearing surfaces in nuclear rockets where there is limited or no exposure to oxygen and where the operation is for relatively brief periods of time.

DESIGN CRITERIA

Rolling-contact bearings, gears, and other parts in sliding and rolling contact must be designed for minimum heat generation and maximum heat

rejection by conduction and must include substantial internal clearance to allow thermal expansion. Wherever possible the materials of construction should be alloys based on hexagonal close-packed metals, which can be improved further with helpful microstructural inclusions. Solid lubricants can be used as coatings on all operating parts, but they are most commonly and effectively employed on the cage (retainer) of rolling-contact bearings. PTFE and MoS_2 are the two most useful solid lubricating materials. Also, MoS_2 can be used as a constituent of a solid body as well as applied in films bonded with phenolic resins, sodium silicate, or other bonding agents. A surface to which a solid film is applied should be roughened or have surface recesses. PTFE compositions need fillers such as glass fibers to prevent cold flow; the use of PTFE at substantial surface speeds should be avoided in vacuum because of the poor heat-transfer properties. Metal fillers and backing can reduce the heat-transfer problem with polymers.

Dynamic seals are not effective for sealing atmospheric and higher pressures against space vacuum. Molecular flow seals can be useful, however, if the maximum pressure in the bearing housing is around 10^{-3} millimeters of mercury. Leakage can be predicted according to the kinetic theory of gases. Conventional organic lubricants can and should be used when they can be adequately sealed with molecular flow seals. The bearing cavity would thus be at the vapor pressure of the lubricant, and any mechanical factors that would raise the operating temperature would make such a system of very limited value because the lubricant vapor pressure can easily exceed the limiting pressure for the use of molecular flow seals. The use of organic fluids in addition to solid film lubricants is not a good practice. The organic fluids will be preferentially adsorbed on the surfaces of the solid lubricant particles and the base metal and will greatly reduce the endurance life of the solid film by adversely affecting the adhesion and cohesion of the film. The gel structure or fillers in greases have no significant effect on the rate of evaporation for the lubricating liquid.

RECOMMENDED PRACTICES AND ACCEPTABLE PROCEDURES

The literature cited in the references contains a myriad of isolated recommendations for the lubrication of space devices that are frequently conflicting. A notable effort to assemble a rationally organized series of recommendations is contained in reference 35. In some matters the material recommendations of reference 35 are in conflict with the suggestions presented herein, but there is general agreement with that more comprehensive document.

Evaporation of Lubricants

The evaporation of organic lubricants may be prohibitive in direct exposure to space vacuum. Methods of determining evaporation in laboratory experiments is the subject of a survey reported in the appendix.

Where lubrication can be provided by the vapor at modest temperatures, molecular flow seals can reduce evaporation and thus enable practical operation for long periods (e.g., 1 yr). Useful fluids include silicones, mineral oils, and polyphenyl ethers. It frequently is most convenient to use these fluids in greases or to employ high molecular weight polymers (waxes and plastics), such as PTFE. Evaporation is less with higher molecular weights within classes of materials.

Inorganic lubricant formulations based on MoS_2, gold, silver, gallium, and CaF_2 have evaporation rates that are several orders of magnitude less than the best of the organics. Some inorganic compounds that have lubricating properties (e.g., PbO and PbS) dissociate in vacuum (300° to 350° F at 10^{-7} mm Hg) and should be avoided.

Materials for Bearing Surfaces

Conventional materials such as hardened 52100 and 440-C can be employed in rolling-element bearings, but the danger of surface cold welding will be reduced if Stellite Star-J or a nonhomogeneous tool steel Circle-C is utilized for rolling elements and/or races. Alloys for vacuum service having microinclusions of compounds that inhibit surface-welding are being developed. They may have greater susceptibility to fatigue failure in high load applications than conventional bearing steels. Free-machining alloys usually have similar properties. Austenitic stainless steels and other homogeneous alloys should be avoided for sliding or rolling contacts because of surface welding tendencies. Dimensional stability with thermal cycling is an important requirement for mechanical parts that should also prevent the use of austenitic stainless steels. High hardness and high elastic modulus are desirable to minimize surface adhesion but are not exclusively required properties. A hardness of Rockwell-C55 is considered mandatory to prevent brinelling. Where high loads are encountered, a high elastic modulus may result in undesirable stress levels.

Filled plastic compositions of polyimide-, epoxy-, and PTFE-base materials can be useful for retainer materials and idler gears to supply transfer films where there is unidirectional rotation and both ambient temperatures and frictional heating are modest. The PTFE-base materials are most common.

Thin gold or silver films on metal retainers (e.g., Circle-C) have given extended performance in industrial vacuum applications for years. The key to good frictional performance is a thin film (<0.0005 in. thick), a hard substrate, and, in some cases, additives (e.g., Ni, In, and Co in Au, as discussed in ref. 13).

Solid lubricant films that are extremely thin (<10^{-5} in.) can be applied on all bearing surfaces (e.g., burnished MoS_2 alone), but usually coating only the retainer with a somewhat thicker film (>2×10^{-4} in.) is the preferred practice for other than low-amplitude oscillating motion.

Coated retainer surfaces should be roughened (ref. 37) or have reservoirs, and the type of coated metal is significant (e.g., Mo containing alloys for MoS_2). Sodium silicate bonded MoS_2 coatings and phenolic containing resin bonded MoS_2 coatings are typical commercial coatings considered useful. Recently developed MoS_2 films containing soft metals such as Au and Ag in the inorganic binder formulations are reported to have useful properties for aerospace applications (refs. 38 and 39).

Component Designs

Angular contact ball bearings with self-lubricating retainer materials are presently most useful. With small axial preload, bearing pairs allow precision support with tolerance for internal thermal expansion by change in contact angle. Minimum heat generation is obtained with open-race curvatures, such as 54 to 58 percent rather than standard 51 to 52 percent. High frictional rolling-element bearing types (e.g., needle bearings) should be avoided. Internal clearances should be as liberal as possible.

Nonmetallic retainers may require metallic support shrouds for high rotative speeds. Outer race piloted retainers are advantageous for high speeds because they tend to be self-balancing and may reduce heat dissipation problems. The most conventional type of retainer shroud, however, is limited to configurations employing inner race piloted retainers.

Sliding bearings need self-lubrication capability obtainable with solid lubricants as films or as constituents in the bearing composition. Materials such as PTFE composites and similar self-lubricating compositions and the solid films mentioned previously are useful. Ceramic-type materials also have potential. Adequate clearances and removal of wear debris are important considerations.

Present use of gas bearings is limited to gyro-gimbal bearings for missile control systems with short operation period requirements. The use of a closed-cycle system may make extended use of gas bearings feasible (ref. 40).

Magnetically supported shafts are of extreme interest. The present state of development involves excessive weight for practical use. Intensive development appears worthwhile (ref. 41).

Gearing and other mechanical parts must also be designed with consideration for minimum friction, effective heat dissipation, thermal expansion (ample clearances), optimum materials to limit surface adhesion, and best utilization of the lubricants selected (ref. 42).

Suggestions on the designs of molecular flow seals are contained in references 12, 43, and 44.

Sliding electric contacts frequently utilize a semiconductor, MoS_2, as a lubricating constituent in the contacting materials. Such materials appear to be useful, but there is much room for improvement in this problem area (refs. 1 and 35).

PROOF TESTING OF COMPONENTS

There is no single test procedure that can adequately assure the succesful performance of lubricated components in space environment. Specific procedures for testing the various components should be considered for each type problem.

Freedom from contamination by extraneous materials that have lubricating capabilities (such as diffusion pump oils and degradation products from electrical insulation) is an absolute requirement for a test system. Freedom from contamination can be verified by the wetability of surfaces after they have been removed from the vacuum chamber by using a drop of distilled water. When, as is usually the case, evaporation of a lubricating material is important, a condensing surface with a high capture coefficient (e.g., a liquid N_2 cooled copper plate) should be used adjacent to the component tested. The geometry of the test installation should, as far as possible, duplicate the design installation in that the leakage conductance for evaporating material would be the same. Temperatures must be measured on the component (e.g., stationary bearing race) being tested. Pressures should be measured in the test chamber adjacent to the test. The pressure level for space simulation should be 10^{-9} or less mm Hg except where special considerations are indicated (e.g., a low orbit for the vehicle).

Accelerated testing is often a requirement but must be done cautiously. An understanding of the probable modes of failure will help in selecting a reasonable accelerated test procedure. For example, bonded solid lubricant films usually fail after a finite number of stress cycles with reasonable independence from frequency effects. Therefore, testing may be done at higher frequencies (speeds) as long as other considerations are not significantly altered. If evaporation is expected to cause failure, acceleration can be achieved by operation at higher temperatures for the lubricated part; again, other considerations should not be significantly altered. Any proposal for accelerated testing should be carefully reviewed by lubrication specialists.

CONCLUDING REMARKS

The discussion presented represents a summary of design criteria for consideration in space vehicle lubrication problems. This technical area is not yet sufficiently developed to allow the publication of designer handbook data. With ingenuity and an understanding of fundamental concepts, however, a competent designer can provide rotating equipment to satisfy most present needs for vacuum lubrication. Much meaningful research is now being accomplished in this area and the designer's task will soon become less difficult.

APPENDIX

SURVEY AND DETERMINATION OF VACUUM EVAPORATION

CHARACTERISTICS FOR LUBRICATING MATERIALS

One of the problems associated with the use of lubricating materials in the environment of space is that of weight loss in vacuum. There are substantial differences of opinion as to the best type of experimental methods and of equipment to be used in studying this problem area as well as to the most significant method of reporting the data. Furthermore, the fundamental processes (such as evaporation) that are usually considered to occur are not always recognized as such.

A questionaire containing 33 questions pertinent to the problem area was sent to over 50 organizations. The questionaires were directed to those individuals in the organization known to be research or development workers with technical responsibilities in the problem area in order to obtain the best technical opinions available. There were 33 written responses, 30 of which were accompanied by completed questionaires. A listing of those who responded with a completed questionaire, a summary of responses to the questions, comments rendered pertinent to the question, and a summation are presented in the following pages.

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TABULATION OF QUESTIONAIRE RESULTS

The questionaires summarized below were completed by individuals who were divided among various academic backgrounds as follows: engineering, 10; physics, 4; metallurgy, 4; chemistry, 11.

When several individuals of different backgrounds prepared a single questionaire or where an individual had major training in several fields, fractional numbers were used. Thus the weighted response given is the same as the total of responses received. Where no response to a question was indicated, it was not included in the tabulation. Only those who indicated no opinion were used as the basis for the tabulation in that column.

Question	Yes	No	No opinion
1. Are you familiar with the classic work of Langmuir, Knudsen, Hickman, and Dushman on evaporation and vapor pressure?	27	2	1
2. Would the work of those investigators provide an adequate basis for defining an evaporation experiment?	22	3	5
3. In space simulated (vacuum) experiments, are the Langmuir concepts valid in the evaporation process?	19	2	7
4. Can a Knudsen cell (embodying flow through an orifice from vapor pressure to a vacuum chamber) truly represent a space evaporative condition?	11	14	5
5. Are outgassing, evaporation, and pyrolytic degradation three distinctly different processes?	27	2	
6. Is ambient pressure important in the evaporation process?	24	2	2
7. In the evaporation process, is exposed surface area of the evaporating material important?	26	4	
8. Should evaporation data be presented as weight loss per unit of exposed surface area rather than percent weight loss?	24	2	2
9. Is the evaporation process in vacuum applicable for high molecular weight polymeric materials?	12	11	6

Question	Yes	No	No opinion
10. Is vessel geometry important in evaporation studies, for example, do vessel walls above the outer edge of sample restrict evaporation?	26		3
11. Are direct temperature measurements an absolute requirement in evaporation experiment?	17	9	2
12. Are indirect temperature measurements acceptable, such as by a calibrated thermocouple adjacent to the evaporating material?	13	13	2
13. Is correlation of evaporation data with the calculated values based on the Langmuir equation an adequate basis for judging the validity of the data?	10	9	8
14. Can weight loss data obtained at temperatures above the threshold of pyrolytic degradation be used as a basis for evaluating evaporation rates at much lower temperatures?		25	3
15. Are energies of the chemical bonds in a molecule important to evaporation rates at temperatures where there is no pyrolysis, for example, in a hydrocarbon and its fluorocarbon analog?	12	14	3
16. In simulating space conditions, should provision be made to remove (condense) evaporated species from the system to prevent return of evaporating materials to the parent surface?	28		
17. Will emissivity between the evaporating surface (100° to 1000° F) in a vacuum and a cryogenic condensing surface (-200° F) in close proximity (1 to 2 in.) influence the real surface temperature of the evaporating material?	20	2	7
18. Is diffusion important in the evaporation process with liquids?	18	8	2
19. Is diffusion important in the evaporation process with solids?	21	4	4
20. If the answer to question 19 is yes, is diffusion important for homogeneous materials?	14	8	4

Question	Yes	No	No opinion
21. Is diffusion important to the evaporative process of hetergeneous materials?	22		4
22. If diffusion is important, is the process dependent upon surface area?	23		3
23. Are all gas-solid processes dependent upon the solid surface area, that is, if in oxidation a weight increase is noted or in evaporation a weight loss noted, are these areas dependent?	25	1	4
24. If diffusion is important, is specimen geometry also important?	25	2	2
25. With materials such as oils, greases, and solid polymers, can three processes occur in vacuum, evaporation, diffusion, and pyrolytic degradation?	27	1	1
26. Does a TGA apparatus (thermogravimetric analysis) without modification give a system which simulates conditions encountered in space with a material which is evaporating?	2	18	10
27. With those materials which are poor thermal conductors, do temperature gradients exist from the surface to within the material when such a material is radiantly heated?	26	1	2
28. If the answer to question 27 is yes, does the surface become of prime importance in the evaporation and degradation of materials since the energy for such processes will be higher at the surfaces?	24	1	2
29. In the evaporation of polymers are only monomers lost?	1	21	7
30. Can higher molecular weights than monomers evaporate from polymers?	24		6
31. Would the use of a mass spectrometer in evaporation experiments be desirable?	26		2

Question	Yes	No	No opinion
32. If the answer to question 31 is yes, can it be used to distinguish between evaporation and degradation based on the fact that the ion source of the mass spectrometer will fragment such materials as the oil and polymer molecules that evaporated?	17	4	5
33. If the answer to question 31 is yes, should the mass spectrometer be placed as close as possible to the source of evaporating material to avoid recombinations and condensation on other surfaces which might promote such recombinations?	20		7

COMMENTS ON QUESTIONS

In answering the questionaire, many individuals felt that some comments should accompany their answers. All the comments made were summarized and are presented for each question of the questionaire. The comments are not necessarily representative of the majority of opinions expressed but are merely a condensation of comments by people who wished to expand on their yes or no replies. The numbers refer to the question listed.

2. (a) Good starting point.
   (b) Definition of evaporation.
   (c) Providing only evaporation takes place.

3. (a) Only if ambient pressure is sufficiently low.

4. (a) Provided all anomalies are resolved.
   (b) One could be designed.

5. (a) All three processes may occur simultaneously.
   (b) Different types of bond rupture are involved in the three processes.

6. (a) Down to pressure when the mean free path equals the container dimensions.
   (b) At pressures to 10^{-5} torr.
   (c) Ambient pressure is important until it is reduced to one-tenth that of the vapor pressure.

7. (a) Exposed surface area is not important to evaporation rate but is in considering total weight loss.
   (b) There is no reason for surface area to be an experimental variable.

8.(a) Yes, but rather difficult because real area is unknown.

9.(a) Polymeric materials may contain a variety of bound and semibound chunks of molecules, which would probably be released irreversibly at various pressures and temperatures.
  (b) Possible; however, frequently the molecular weight is so high and vapor pressure so low that thermal degradation occurs before evaporation.

10.(a) Yes, because collisions of evaporating molecule with vessel wall will reduce amount of material lost.
  (b) Vessel wall can act as a baffle.
  (c) Labyrinth vessel can be used to reduce evaporation.

12.(a) Yes, if they give the temperature of evaporating surface.
  (b) Yes, if properly calibrated.
  (c) Yes, results must be interpreted carefully, however, because heat loss through vaporization would cool the surfaces.

13.(a) Yes, for homogeneous materials.
  (b) Yes, if Langmuir data were not originally obtained by converse process.

14.(a) No. As indicated in question 5, you have two distinctly different processes.
  (b) Depends on the definition of threshold of pyrolytic degradation.

15.(a) Hydrogen bonding between molecules could have an effect.

16.(a) Importance of this provision depends upon conditions under which the process takes place.

17.(a) It is possible to adjust heat input to maintain constant temperature.

18.(a) It could be for a mixture of liquids.
  (b) In liquids, surface evaporation results in a lowered surface temperature, and diffusion in the liquid is required to restore temperature equilibrium.
  (c) Fick's laws of diffusion and evaporation use completely different units of measure; however, both processes are temperature dependent.
  (d) Function of concentration.

19.(a) This question can be answered either way depending upon the materials involved.
  (b) Not for a pure crystalline solid, but it could be for plasticized polymer.

20. (a) It may be if evaporation is a strong function of the particular crystalline surface and replenishment is by diffusion.

22. (a) Process also depends upon mass and geometry of specimen.
    (b) It depends upon the relative importance of the two processes.
    (c) The rate of mass loss due to diffusion would be proportional to surface area.
    (d) Dependent to some degree.

23. (a) There are exceptions to this situation such as materials with high dissociation pressures.
    (b) Processes also depend upon mass and geometry of specimens.
    (c) It depends upon the rate controlling process.

24. (a) Yes, with surface area and specimen thickness being the more important geometric parameters.

25. (a) A fourth process could be added, i.e., degassing.

26. (a) There appears to be no generally accepted definition of a TGA apparatus.
    (b) Source to wall would not be long enough.

27. (a) Depends upon thickness of sample and whether it is heated from one side or both.
    (b) Depends upon the heat flux, the thickness, and the substrate thermal properties

28. (a) The region of highest temperature would be the region of highest activity whether it is evaporation, degradation, or diffusion.
    (b) Dangerous to generalize regarding one factor.

29. (a) It would depend on whether the material could be only a vapor at the test temperature.
    (b) Polymers contain low molecular weight fragments, plasticizers, and entrapped gases and vapors which must be considered.

32. (a) Depends upon method of degradation.
    (b) Depends upon nature of evaporating material.

SUMMATION OF QUESTIONAIRE

The following summary remarks are based on the responses to the questionaire:

1. Most individuals polled were familiar with the classic work on evaporation reported in the literature and agree that the concepts of Langmuir are valid in defining an evaporation experiment.

2. A Knudsen cell generally does not represent a space evaporative condition but with proper modifications and/or precautions it can be useful.

3. Outgassing, evaporation, and pyrolytic degradation are three distinctly different processes.

4. Ambient pressure and exposed surface area are important. Evaporation data should be presented as weight loss per unit area rather than percent weight loss.

5. Vessel geometry is important to the evaporative process.

6. Mixed views are held concerning temperature measurements of specimens. Some feel direct measurements are necessary, others feel indirect measurements with proper calibration are adequate.

7. Pyrolytic degradation data cannot be extrapolated to give evaporation rates at lower ambient temperatures.

8. It is important to remove evaporating species from the system.

9. In general, diffusion is significant to the evaporation process and diffusion is dependent upon surface area.

10. Specimen geometry is important.

11. With oils, greases, and solid polymers in vacuum, all three processes, evaporation, diffusion and pyrolytic degradation, can occur.

12. A standard unmodified TGA apparatus does not simulate space conditions for a material evaporating.

13. Thermal gradients do exist in radiant heating of materials which are poor thermal conductors. In such materials, surface area is important.

14. Higher molecular weight species than monomers evaporate from polymers.

15. A mass spectrometer would be a definite asset to evaporation experiments.

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